Tetrahedron Letters No. 2, pp. 1-3, 1960. Pergamon Press Ltd. Printed in Great Britain.

SUBSTITUENT AND SOLVENT EFFECTS ON THE $n \rightarrow \pi^*$ ('U ← 'A) TRANSITION IN ALIPHATIC CARBONYL DERIVATIVES: EVIDENCE FOR HYPERCONJUGATION IN THE EXCITED STATES OF MOLECULES

C. N. R. Rao, J. Ramachandran* and G. K. Goldman**

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, India

(Received 15 December 1959)

WE have been investigating structural and solvent effects on the $n \rightarrow \pi^*$ transition[1] of the carbonyl group, particularly in the aliphatic derivatives. It has been noted earlier[2,3] that substituents capable of donating electrons to the π-conjugated system by resonance interaction shift the $n \rightarrow \pi^*$ transition to lower wavelengths. In the $n \rightarrow \pi^*$ transition of the carbonyl group, the electronic charge is transferred from the oxygen to the carbon. Groups like the halogens, $-OCH_3$ and $-NH_2$ when attached to the carbon atom cause a very large decrease in the wavelength. Interestingly enough, aliphatic carbonyl compounds (RCOR' where R = CH_3) with R' as H, CH_3, C_2H_5, i-C_3H_7 and t-C_4H_9, show the $n \rightarrow \pi^*$ transition bands at 2910,

---

* University of California, Berkeley, Calif., U.S.A.

** Purdue University, Lafayette, Indiana, U.S.A.

[1] J. W. Sidman, Chem. Rev. **58**, 689 (1958).

[2] A. Burawoy, J. Chem. Soc. 1177 (1939).

[3] S. Nagakura, Bull. Chem. Soc. Japan **25**, 164 (1952).

2765, 2775, 2835 and 2860 Å respectively in a hydrocarbon solvent. There is a large decrease in the wavelength going from R'=H to R'=CH_3 and then on there is a progressive increase in the wavelength in the series. This suggests that when both R and R' are methyl groups, there may be some type of resonance interaction by electron donation. This interaction decreases when R' is H or any other alkyl group. Inductive interaction cannot explain this trend in the wavelengths since trifluoroacetone (R'=CF_3) shows this transition at 2775 Å in o-octane. If the extra resonance interaction when both R and R' are methyl groups is considered to be by C-H hyperconjugation, then, the variation of the $n \rightarrow \pi^{*}$ band maximum with R' is in the Baker - Nathan order. This order is maintained in solvents of varying degree of polarity and/or hydrogen bonding. So, this trend may be taken as evidence for hyperconjugation in the excited states of molecules. We have studied this transition in a number of aliphatic ketones and a treatment similar to that of Kreevoy and Taft[4] should be possible.

In general it may be said that the effect of alkyl groups on the near ultra-violet absorption spectra of aromatic compounds is not consistent. The evidence presented from this study for resonance (possibly by hyperconjugation) in the alkyl groups in the excited states of molecules seems to be foolproof because, (i) the molecules studied are aliphatic and so no other type of resonance interaction can occur, (ii) in the molecules studied hyperconjugative resonance has been shown[5] to be unimportant in the ground state, (iii) the unusual electronic transition employed is very structure

---

[4] M. M. Kreevoy and R. W. Taft, Jr., *J. Amer. Chem. Soc.* **77**, 5590 (1955).

[5] C. N. R. Rao, G. K. Goldman and C. Lurie, *J. Phys. Chem.* **63**, 1311 (1959).

sensitive, and (iv) similar trends are observed in different solvents of varying degree of polarity and/or hydrogen bonding.

All the ketones show increasing solvent blue shifts[1] with the increasing polarity and/or hydrogen bonding ability of the solvent. In the series of aliphatic carbonyl compounds (RCOR' with R=CH_3), the solvent blue shift is maximum when R'=CH_3, in all the solvents studied. At least part of this effect may be due to the slightly larger permanent dipole moment of acetone compared to the other derivatives. Another explanation for this effect can be based on the extra resonance interaction of the two methyl groups which may result in a more complex charge distribution of the acetone molecule in the excited state. Then, by the Franck - Condon principle the solvation energy in the excited state of acetone will be considerably different from others.

Further work is in progress and it is hoped to publish a detailed report of the substituent and solvent effects in the near future.

We wish to thank the authorities of the Departments of Chemistry, University of California and Purdue University for providing facilities for research.